NATIVE SULFUR IN SEDIMENTS FROM KT BOUNDARY SITES OF THE BRAZOS RIVER, TEXAS. Dieter Heymann<sup>1</sup>, Thomas E. Yancey<sup>2</sup>, and Mark H. Thiemens<sup>3</sup>, <sup>1</sup> Department of Geology and Geophysics, Rice University, Houston Texas 77251-1892, USA; <sup>2</sup> Department of Geology and Geophysics, Texas A&M University, College Station Texas 77843-3115, USA; <sup>3</sup> Department of Chemistry & Biochemistry, University of California San Diego, La Jolla California 92093-0356,

Native sulfur [1] was serendipitously discovered in samples from five locations of the Cretaceous-Tertiary (KT) boundary complex of the Brazos River, Texas. The amounts ranged from about 1 to 400 ppm. The isotopic composition of the S<sup>O</sup>,  $\delta^{33}$ S = -12.97 ‰,  $\delta^{34}$ S = -24.89‰, and  $\delta^{36}S = -46.4$  %, ruled out an origin from the Chicxulub impactor, because all extraterrestrial SO studied to date had δ-values close to zero [2]. Our preferred interpretation is that this SO was formed by a local and transient "bloom" of sulfur-reducing bacteria, but other explanations cannot be ruled out.

Twenty-five samples from the Brazos-1 section (BR1; a trench in the west bank of the river); four, one, five, and three samples respectively from the nearby riverbed sections RB1, RB2, RB4a, and RB4b; and four samples from the Darting Minnow Creek (DMC) section of the Brazos complex were treated with toluene for the extraction of S<sup>O</sup>, the amounts of which were determined by High Performance Liquid Chromatography. One sample from the spherulitic bed from Beloc, Haiti was included in this study [3]. It contained no S<sup>o</sup>. Table 1 presents the results for all samples which contained SO. The results for the BR1 section are also shown in Figure 1, together with iridium anomalies determined by others [4]. The isotopic composition of SO extracted from sample BR39 was determined mass-spectrometrically. [details in ref. 2].

At BR1, the largest SO contents occur in SCB, a unit which contains spherules, shell hash, and clay mud. The spherules are thought to have been formed by the impact into the Chicxulub section; they are known to contain calcium sulfate [5]. The other occurrences of SO are in HCS

(hummocky sandstone), TSU (narrow transitional bed from sandstone to a more carbonate-rich sediment), SB a thin sandy bed, and MMS (a mudstone), but always at, or near an iridium anomaly. At the other sections, the S<sup>O</sup> always occurs in spherule-bearing sediments.

Our preferred interpretation does not require transportation of SO from Chicxulub to Brazos, but suggests the local formation of S<sup>O</sup> from sulfate by sulfate-reducing bacteria. It has long been known that very large and negative isotopic shifts can occur during this reduction, which would account for the observed negative δS values, especially because the  $\delta^{34}$ S-value of the parent sulfate appears to have been in the comparatively low positive range of +5 to +10 ‰ [5]. Sulfate was provided by the spherules from the Chicxulub impact, organic matter was locally available, and the bacteria were already ubiquitously present in the sediments. There was probably a short, transient "bloom" which ended when either the sulfate or the organic matter became exhausted.

One alternative hypothesis is that SO was "exhumed" from the Chicxulub section and transported by the impact event to Brazos. This is unlikely because no SO has been reported in the Chicxulub section. Another hypothesis is that the SO formed from SO2 and H2S in the atmospheric plume from the impact.

**References:** [1] In the following, S<sup>O</sup> will represent native sulfur. [2] Gao X. and Thiemens M. H. (1991), GCA 55, 2671. [3] Sample donated by Dr. V. L. Sharpton. [4] Ganapathy R. et al. (1981) EPSL 54, 393; Rocchia R. et al. (1996) In: GSA Spec. Pap. 307, 279. [5] Chaussidon M. et al. (1996) In: GSA Spec. Pap. 307, 250.

	See figure 1 for designations of Units of BR1.					
SECTION/ UNIT	SAMPLE	S <sup>o</sup> (ppm)	SECTION/ UNIT	SAMPLE		
RR1/MMS	DD 20	1.2	PR1/GSR	RD45		

SECTION/ UNIT	SAMPLE	S <sup>o</sup> (ppm)	SECTION/ UNIT	SAMPLE	S <sup>O</sup> (ppm)
BR1/MMS	BR28	1.2	RB1/GSB	BR45	4.3
BR1/MMS	BR26	1.3	RB1/GSB	BR46	18.2
BR1/MMS	BR36	2.3	RB1/BCB	BR9.1	5.8
BR1/SB	BR1	4.4			
BR1/SB	BR2	8.6	RB2/CB	BR47	14.5
BR1/TSU	BR38	4.5			
BR1/HCS	BR40	0.9	RB4a/SCB	BR48	1.1
BR1/SCB	BR39	62.7	RB4a/SCB	BR49	12.6
BR1/SCB	BR42	409	RB4aSCB	BR50	2.1
BR1/SCB	BR43	209	RB4a/SCB	BR51	≤ 2
BR1/SCB	BR44	158	RB4a/SCB	BR52	2.5
DMC1/SCB	BR56	1.5	RB4b/SCB	BR53	1.2
DMC1/SCB	BR58	0.6	RB4b/SCB	BR54	0.6
DMC1/SCB	BR59	2.1	RB4b/SCB	BR55	9.0

TABLE 1. Sulfur contents of samples from the Cretaceous-Tertiary complex of the Brazos River.

NATIVE SULFUR AT BRAZOS: Heymann et al.

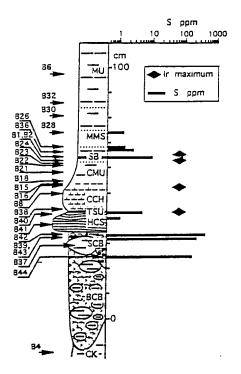


Figure 1. Stratigraphy, sulfur content and iridium maxima in sediments of the Brazos-1 section. Where multiple measurements were done for a given bed, only the largest values are shown. Where no bar graph is shown, the corresponding sample contained zero sulfur. Note that the largest of all S abundances occur in the SCB bed which is rich in spherules and shell hash. Note also the coincidence of Ir anomaly and sulfur at the base of unit CCH, a calcareous clayey unit. No sulfur was found in sediments from the CMU bed, a calcareous mudstone, where several investigators found a small Ir abundance maximum [4]. Sulfur occurs in and a short distance above the SB bed near which Ir maxima were found [4]. Zero datum is placed at the top of the Corsicana/Kemp (CK) formation, the (Chicxulub) event-defined KT horizon; the paleo-defined KT boundary is located in bed SB. Other units of the section are: BCB = basal conglomerate; HCS = hummocky sandstone; TSU = transitional zone from HCS to CCH. MMS and MU are mudstones.